

PATENT SPECIFICATION

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(54) PROCESS FOR CONTINUOUS PREPARATION

(71) We, MITSUBISHI GAS CHEMICAL COMPANY INC., a Japanese Body Corporate of 5-2, 2-Chome, Marunouchi, Chiyoda-Ku, Tokyo, Japan, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:
This invention relates to a process for continuously preparing aromatic aldehydes by reacting aromatic hydrocarbons with carbon monoxide in the presence of hydrogen fluoride and boron trifluoride.
On laboratory scale, the reaction of synthesizing aromatic aldehydes from aromatic hydrocarbons and carbon monoxide using hydrogen fluoride and boron trifluoride as catalysts can be carried out quite quickly and selectively, though variations occur depending on the nature of the starting hydrocarbons. The said reaction is a relatively high exothermic reaction, but when the reaction temperature becomes higher, the resulting aldehydes bring about such side reactions as polymerization, condensation, etc. due to the actions of hydrogen fluoride and boron trifluoride, with the result that the yields of the end products are decreased. Accordingly, the heat generated in said reaction should be removed as quickly as possible. However, when the reaction is effected on industrial scale by use of an ordinary tank-type reactor, a heat transfer area sufficient for required heat removal cannot be secured by only the surface area of the reactor, and therefore the reactor should necessarily be equipped separately with internal or external heat exchangers. Because corrosive materials are being treated, however, the provision of such heat exchangers is not desirable, and the size of the reactor used is preferably made as compact as possible. In the present invention, the above-mentioned disadvantages are overcome by quickly removing the heat

generated in the reaction thereby maintaining the reaction system at a low temperature.

The present invention provides a process for the continuous production of aromatic aldehydes which comprises passing a reaction liquid comprising an aromatic hydrocarbon, hydrogen fluoride and boron trifluoride through a tubular reaction zone capable of providing a turbulent flow of the reaction liquid therein, while feeding carbon monoxide to the reaction zone at a plurality of different locations spaced apart in a direction cocurrent to the flow of the reaction liquid.

Preferably the tubular reaction zone is provided by means of a pipe reactor. A pipe reactor gives various advantages as mentioned below.

By selection of the tube diameter, a required tube surface area corresponding to the reactor volume can be secured as a heat transfer area by dipping the reactor in the cooling medium. The gas-liquid contact can successfully be accomplished by selecting such a tube diameter that the flow rates of fluids flowing inside the tube can be made sufficient to cause a turbulent flow inside the tube. If necessary, the gas-liquid contact effect can be more enhanced by providing line mixers or properly shaped obstacles within the reactor.

We have found that when the carbon monoxide is fed to the reactor in the above-specified manner, the aromatic hydrocarbon and carbon monoxide can be uniformly reacted over the whole space of the reactor without causing any local reaction, thereby making it possible to avoid a local temperature increase. As the carbon monoxide is absorbed in the reaction liquid, fresh carbon monoxide in an amount corresponding to the amount absorbed is successively fed, whereby the proportions of the reaction liquid and the carbon monoxide become al-

ways constant to make it possible to decrease the dead space of the reactor and to greatly increase the volume efficiency of the reactor. The larger the number of different locations of the reaction zone (inlets of a reactor) at which the carbon monoxide is fed, the greater the effect obtained. Preferably at least five such locations are preferred. Ordinarily, however, sufficient effect for most practical purposes can be obtained when the carbon monoxide is fed at from 3 to 10 locations. The carbon monoxide is desirably fed at such locations that the carbon monoxide gas hold-up in the reactor can be made as uniform as possible over the whole space of the reactor, taking into consideration the rate of carbon monoxide absorbed in the reaction liquid inside the reactor. It is therefore preferable that the carbon monoxide is fed not through locations which have been positioned at equal intervals over the whole length of the reactor but at locations which have been so positioned that the intervals between locations in the part of the zone where the before-half stage of the reaction is effected, where the reaction rate is high, have been made shorter than those between the locations in the part of the zone where the latter-half stage of the reaction is effected, where the reaction rate is low.

The amount of carbon monoxide fed at each location is not required to be controlled, in general, and the desired object can be accomplished by dividing the total amount of carbon monoxide required to be fed equally among the individual feed locations.

The feed locations conveniently take the form of nozzle inlets at fixed portions of the reactor, no sophisticated equipment being necessary. Desirably, the nozzles are so positioned that the gas-liquid contact in the reactor can be conducted as effectively as possible.

In the present invention, the reaction temperature is below 0°C., preferably 0° to -20°C., and the reaction pressure is 5 to 50 kg/cm², preferably 10 to 30 kg/cm². The amount of the carbon monoxide is about 0.7 to 1.0 mole per mole of the starting aromatic hydrocarbon. The amounts of the catalysts are such that 3 to 6 moles of hydrogen fluoride and 1 to 1.5 moles of boron trifluoride are used per mole of the starting aromatic hydrocarbon, and the molar ratio of hydrogen fluoride to boron trifluoride is preferably 4-10 : 1. The linear velocity and the gas-liquid ratio in the reactor are especially important factors for this reaction. The average linear velocity in the reactor should be selected in the range of 1-7 m./sec. When the velocity is lower than 1 m./sec., the heat generated in the reaction is not removed sufficiently soon and the dispersion

of gas into liquid is not conducted well. The gas-liquid ratio, that is gas volume/gas volume + liquid volume, is maintained at less than 0.5 throughout the reactor.

The hydrocarbons which may be employed in the practice of the invention include the monocyclic and polycyclic aromatic hydrocarbons such as benzene, naphthalene, phenanthrene, diphenyl, diaryl methanes, alkyl-substituted aromatic hydrocarbons, such as toluene, ethyl benzenes, propyl benzenes, butyl benzenes, hexyl benzenes, etc.

By the present invention, aromatic aldehydes can be produced in high yields from aromatic hydrocarbons and carbon monoxide by use of an extremely simple apparatus. Thus, the technical value of the present invention is markedly high.

Now the present invention will be illustrated in detail by way of an example, with reference to the accompanying drawing showing the flow diagram of one embodiment of the invention.

Example

As the reactor 5 (in Fig. 1; the same shall apply hereinafter), a pipe having a total length of 800 m. was prepared by connecting stainless steel tubes of 30 mm. in inner diameter and 10 m. in unit length. The reactor was dipped in a coolant kept at -20°C. In the blender 1, toluene was blended with hydrogen fluoride and boron trifluoride to form a toluene complex solution, which was then continuously fed through the line 2 to the reactor 5 by means of a high pressure pump, so that the amounts of toluene, boron trifluoride and hydrogen fluoride became 12.5 kg-mol. 13.5 kg-mol. and 67.5 kg-mol. per hour, respectively. On the other hand, 99% purity carbon monoxide containing nitrogen as impurity was fed from the pressure drum 3 under a pressure of 30 kg/cm²G to the reactor, through the inlet of the reactor and a total of seven nozzles distanced from said inlet by 20, 100, 150, 250, 350, 500 and 650 m., respectively. The pressure inside the reactor was maintained under a definite pressure of 25 kg/cm²G by controlling the feed amount of carbon monoxide. The synthesis liquid at the outlet of the reactor was withdrawn through the line 6, and once stored in a gas-liquid separation drum kept under the same pressure as the reaction pressure. In the gas phase, the nitrogen in the starting carbon monoxide was present at a concentrated state, and a part of the gas phase was continuously purged through the line 9. By means of thermocouples inserted in various portions of the reactor, it was confirmed that the reaction liquid was maintained at below 0°C. over the whole length of the reactor, and thus favorable heat removal was effected. The amount of the fed carbon

monoxide was 10.8 kg-mol. per hour; the conversions of toluene and carbon monoxide were 85% and 98%, respectively; and a toluyal aldehyde composed of 96.5% of p-toluyal aldehyde and the remainder of o-toluyal aldehyde was obtained quantitatively from the reacted toluene and carbon monoxide. The side reaction ratio of aldehyde thus obtained was below 0.2%. The synthesis liquid in the gas-liquid separation column was withdrawn through the line 8, and then subjected to thermal decomposition to recover hydrogen fluoride and boron trifluoride and the toluyal aldehyde.

15 Comparative Example

The reaction was conducted under the same condition as in example except that carbon monoxide was fed through only one nozzle spaced apart from the inlet of reactor 20 by the distance of 20 m. In that case, the conversion of toluene was 60% and the side reaction ratio of aldehyde was 1.5%.

When the tank type reactor having 3 times of volume of reactor in example was 25 used, the conversion of toluene was 70% and the side reaction ratio of aldehyde was 1.0%.

WHAT WE CLAIM IS:

1. A process for the continuous production of aromatic aldehydes which comprises

passing a reaction liquid comprising an aromatic hydrocarbon, hydrogen fluoride and boron trifluoride through a tubular reaction zone capable of providing a turbulent flow of the reaction liquid therein, while feeding carbon monoxide to the reaction zone at a plurality of different locations spaced apart in a direction concurrent to the flow of the reaction liquid.

2. A process according to claim 1, wherein said tubular reaction zone is provided by means of a pipe reactor.

3. A process according to claim 1 or 2, wherein the reaction is carried out in such operating conditions that the linear velocity is maintained at from 1 to 7 m./sec. and the gas/liquid ratio is kept at less than 0.5 throughout the reactor.

4. A process according to any preceding claim wherein the carbon monoxide is fed through 3 to 10 different locations.

5. A process according to claim 1, substantially as described in the Example.

6. An aromatic aldehyde obtained by a process claimed in any preceding claim.

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COMPLETE SPECIFICATION

1 SHEET

This drawing is a reproduction of
the Original on a reduced scale.

